

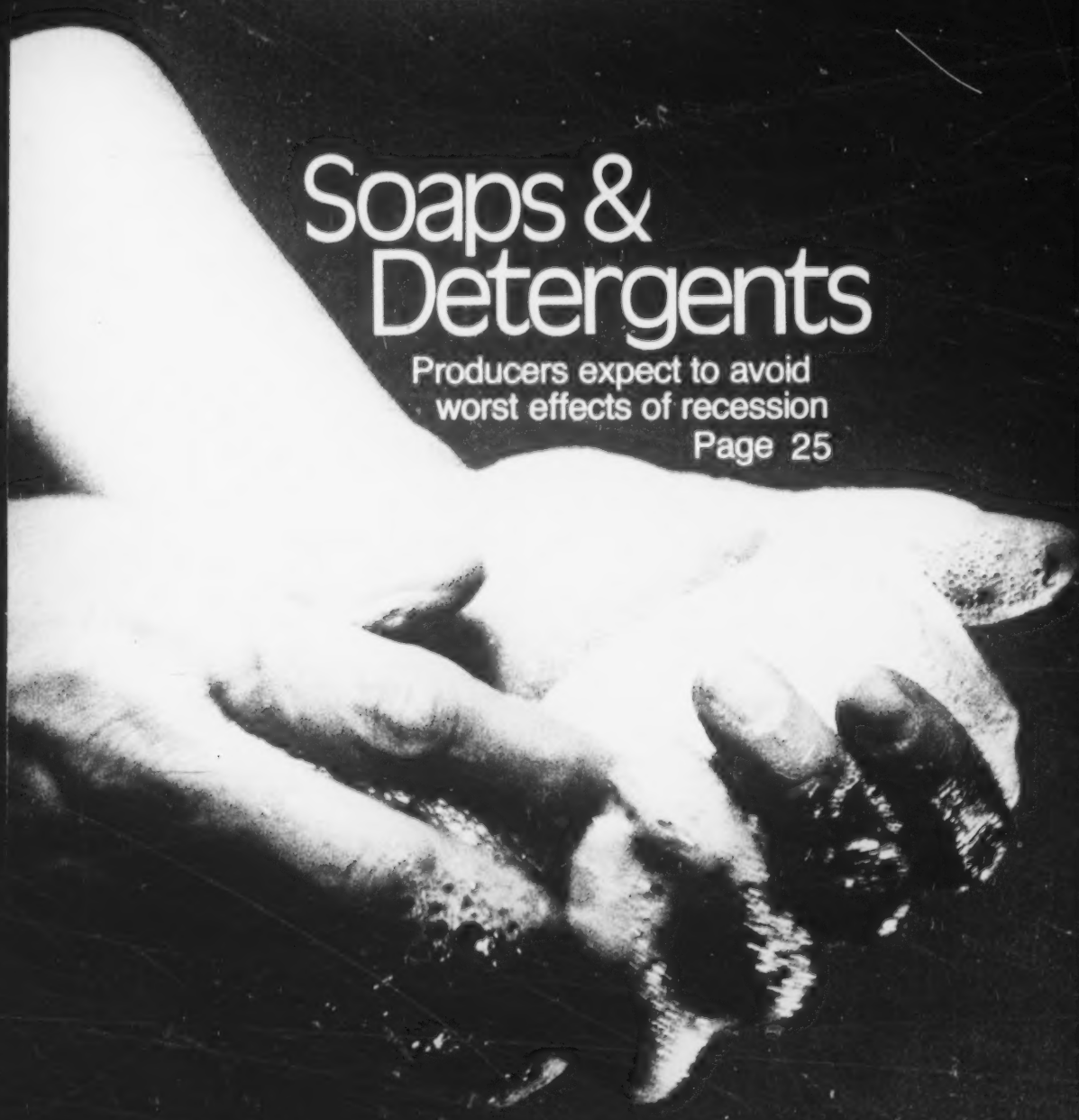
JANUARY 28, 1991

CHEMICAL & ENGINEERING

NEWS

Soaps & Detergents

Producers expect to avoid
worst effects of recession
Page 25



News of the Week

■ Brookings Institution symposium focuses on recent report to the Administration by high-level panel recommending sweeping changes in U.S. space program. **Page 6**

■ Cancer risk of exposure to dioxin may be lower than previously thought, according to new epidemiologic study from NIOSH on industrial workers exposed to high levels of dioxin. **Page 7**

■ Last year's fourth-quarter earnings of many chemical companies are down or flat, reflecting decline in economy. **Page 7**

■ Exxon and Monsanto have merged their thermoplastic elastomer businesses to form a new firm, Advanced Elastomer Systems, with estimated worldwide sales of \$100 million. **Page 8**

■ Belgian chemists develop nonporous aromatization catalyst for *n*-alkanes that may offer new approach for hydrocarbon re-forming. **Page 8**

Cover: Photo by Amy Meyer Phifer

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Business

Process for "clean" reformulated gasoline, ready for licensing to refiners, promises increased engine efficiency, lowered emissions. **Page 11**

German agency is seeking foreign funds for plan to remodel former East German firms into competitive, free-market institutions. **Page 12**

Government

New safety standards expected this year for railroad cars carrying hazardous materials are aimed at improving design and safety features of tankcars. **Page 16**

Science/Technology

Stable, crystalline carbene is isolated by Du Pont researchers, but French chemist, whose work they didn't cite, disputes their claim of first "bottle-able" carbene. **Page 19**

NASA and European Space Agency plan joint Saturn mission to begin in 1996 or earlier. **Page 20**

Quantized transition state is revealed by highly accurate quantum dynamics calculations. **Page 21**

Catalytic, low-temperature, solution-phase oxidation of methane to methanol derivative achieved. **Page 22**

Books

One hundred-plus year history of the chemistry department at the University of Wisconsin, Madison, is a model par excellence; "Readings in Risk" gives readers several viewpoints. **Page 54**

Product Report

Soap and detergent producers look for sales to rise more than 3% this year on the strength of new formulations, more innovative products, and expanding research in spite of the specter of recession. **Page 25**



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LETTERS

CHEMICAL SAFETY

Synthesis of nopinone

Letters to C&EN (Aug. 6, 1990, page 2; Dec. 10, 1990, page 4) have described the hazards associated with the ozonolysis of β -pinene to produce nopinone. While at Purdue University, my colleagues and I successfully ran this reaction several times (up to a 0.5-mole scale; 85% yield) using a Me_2S quench (sixfold excess for 36 hours at ambient temperature).

Recognizing the inherent dangers of this methodology, we developed a

simple, alternative synthesis of nopinone, the full experimental details of which can be found in the *Journal of Organic Chemistry* [55, 1220 (1990)]. Briefly, this one-pot synthesis involves the dihydroxylation of β -pinene using trimethylamine *N*-oxide dihydrate/catalytic OsO_4 , followed by oxidative cleavage of the diol by NaIO_4 . This reaction proceeds in 66% overall yield.

Steven Weissman

Merck Chemical Manufacturing Division,
Rahway, N.J.

Credit for Unipol process

Recently, I was fortunate to be selected for the ACS Award for Creative Invention. My purpose in writing to you is to correct the citation (C&EN, Nov. 15, 1990, page 44), which states that my "best known work is the invention of the Unipol process." This process, a wedding of many technologies, owes its existence to a team effort. My major contribution to this process was in leading the development of the polymerization catalyst systems. It should also be noted that Unipol is not a single invention, but a body of technology with many inventions whose state of the art is continuously being advanced by us.

In closing, I would like to recognize the important contributions of my colleagues and our customers, which have made the Unipol process a commercial success.

F. J. Karol

Polyolefins Division
Union Carbide Corp.

Chemical sensitivity

This is in regard to the letter by Joseph Irgon on chemical sensitivity (C&EN, Dec. 3, 1990, page 5). During World War II, while taking a course sponsored by the U.S. Army, I, too, was subject to mustard gas exposure, albeit slightly.

The class was designed for those chemists who wished to volunteer for civil defense hazardous chemicals teaching. The course was taught at Purdue University and the graduates were then certified by the Army Civil Defense Corps as "instructors of chemical weapons." We taught block wardens, nurses, doctors, and other notable civilians on how to cope with a poison gas attack.

The first day of the class, all of us were ordered to roll up our sleeves, whereupon one drop of mustard gas was applied to each forearm. The effects were then followed during the course period on each person.

It was surprising to see the extreme differences in chemical sensitivity by different persons. Some received terrible blisters, while others (including myself) had little or no discomfort except a slight blister.

Fred C. Trager

Barberton, Ohio

Divine right of chemists

Attila E. Pavlath's letter (C&EN, Nov. 26, 1990, page 4) in response to Paul Gassman's commentary bothered me greatly. He states: "I have never met anyone in our profession who would have claimed any divine right; they only asked for human decency and fairness." This clever recasting of Gassman's complaint misses the point: Neither divine right, fairness, nor human decency are in any way guaranteed us in this world.

Based on these hypothetical (yet non-divine?) rights, Pavlath complains about the "what have you done for me today?" attitude of employers and sneers at "nonacademic managers." Are nonacademics somehow unworthy of these same elusive rights? I believe rather that these annoying nonacademics have come to grips with a reality that does not provide a causative link between education and pay level.

I do not want or expect ACS to "stand up for the practitioners of chemistry." To whom would they stand up and on whose behalf? What would then differentiate ACS from a union? I expect ACS to act as an enabling resource to enhance



PRODUCT REPORT

Sales of Detergents Growing Despite Recession

Bruce F. Greek, C&EN Houston

In spite of gloomy economic forecasts, soap and detergent producers are expecting to see increasing dollar volume, if not physical volume, as new formulations providing better convenience for consumers improve the value-added component of their products.

Spurred by the rising prices of materials, normal population growth, and the per capita spending for cleaning products that is holding about constant despite the current recession, soap and detergent sales likely will rise more than 3% in 1991. Physical volume may be down, however, because a shift toward concentrated detergents for use in home laundry is thriving. If price margins are maintained, however, 1991 could be a far better year for the soap and detergent industry than current signs would indicate.

Nevertheless, this year could

prove difficult on a volume basis for producers of soap, detergents, cleaners, and personal care products if growth slows as it has in past recessions. Most industry sources, however, expect new formulations, more innovation, and further expansion of research for future development to continue. It is ongoing efforts in those areas that support the many forecasts for increasing sales, even in a year that might have two down quarters for gross national product.

Companies of this global industry will continue to position themselves to use the innovations stemming from worldwide laboratories and engineering offices. Marketing research shows that changing consumer preferences in finished formulated soaps, detergents, and personal care products in this industry where sales in 1991 may exceed \$13 billion offer a reliable trend for the future. Companies that meet current demand changes are having com-

mercial success selling their concentrated powdered detergents, combinations in which a bleaching agent is incorporated into the formulated detergent, and in supplying the various ingredients used in desirable finished products.

The soap and detergent industry moves into this decade modifying its myriad products to adapt to environmental concerns that are gathering momentum each year. The concentrates—superconcentrates, or compacts, or ultras—provide a good example of innovation in the area of environmental concerns. The concentrates are designed to provide equally effective clothes cleaning results, while reducing the amount of packaging required, the load on municipal water systems, store shelf space requirements, and shipping and handling costs.

Current focus in the detergent industry is on development of concentrated powders. But changes also are occurring in liquid detergent products. They, too, are being formulated in higher concentrations, although recent modifications in liquids are not so extensive as in powders. Other laundry aids, especially fabric softeners, are coming to market in more concentrated form, including dilutable-by-the-consumer forms, with the objective of further reducing the number of packages to be disposed of or recycled. Many industry observers expect few other changes resulting from the growing awareness of environmental preservation needs except for the reduction in diluents for products.

It is the pressure for ever better performance at lower cost that is spurring suppliers in the industry to improve the surfactants they offer to formulators. Quality improvement programs are viewed by most suppliers as necessary to retaining cus-

A primer for soaps and detergents

Except for a few, soaps and detergents are physical mixtures of various compounds derived either from natural products or from petroleum and coal tar. The compounds are classed as surfactants, builders, bleaches, and additives.

Each compound goes into a formulated detergent to do a specific job:

- Surfactants hold dirt components in a solvent, usually water, for subsequent removal.
- Builders tie up calcium and magnesium ions to improve surfactant activity.
- Bleaches oxidize other compounds that reduce light reflectivity.
- Additives brighten colors, remove stains, reduce soil redeposition, reduce corrosion of laundry equipment, provide a desirable odor, prevent caking, and speed the mixing and other manufacturing processes.

Production: Total volume of materials produced for soaps and detergents is unknown because formulations generally are proprietary. Active ingredients, diluents, and fillers total more than 10 billion lb.

Producers: About 200 companies actively supply materials and finished soaps and detergents. Chemical companies supply the big majority of surfactants, builders, and other components. Formulators of finished products also may make chemical derivatives for captive use.

Sales: Industry shipments in 1990 are estimated at \$12.8 billion, up 5.9% from 1989.

Manufacture: Diversity of products results from use of the many types of chemical reactions in the several processing steps between basic materials and finished goods. Raw materials include basic petrochemicals, natural oils, phosphorus, chlorine, hydrogen peroxide, and beneficiated ores containing carbonates and silicates.

Prices: Pricing of finished products sold to consumer and industrial markets varies widely. Basic and necessary ingredients, surfactants, averaged 55 cents per lb for 3.8 billion lb sold in 1989, the latest year for which data are available.

tomers. Improved surfactants from these programs allow the concentrates to perform better even when used in smaller quantities.

The higher cost of improved cleaning, more concentrated formulations, and processing changes geared to meet environmental requirements appears to be acceptable to consumers. The value of shipments by the soap and detergent industry in 1990 is estimated by the Department of Commerce to be up from \$12.1 billion in 1989 to \$12.8 billion, an increase of 5.9%. Shipment value of surfactants alone has increased almost as much, up 5.8% to \$3.9 billion.

Last year trade grew faster than total shipments but the basis was much smaller. Soap and detergent exports rose 8.9%, to \$295 million, while imports rose 12%, to \$165 million, according to Commerce figures.

The U.S. market for heavy-duty laundry detergents was about \$3.7

billion in 1990, according to Leo R. McIntyre, an industry specialist in Commerce's office of chemicals. Of the total, 63% was sold as household detergents. Sales of heavy-duty liquid laundry detergents, after doubling in volume during the past five years, now account for more than 40% of the U.S. market. Growth has slowed to about 3% annually, McIntyre says. That is about the same as growth in powdered detergents. Liquid detergents take more than half of sales in geographical areas where phosphate materials are banned as builders in detergent formulations. However, in areas where phosphates are not limited, liquid formulations take only 30% of the market.

Bar soap shipments have grown more rapidly since 1987 than in the earlier 1980s. In 1990, shipments were 980 million lb, with a value of \$1.5 billion, McIntyre estimates. Annual growth since 1987 averages 4.9%. Liquid toilet soaps account for

about 10% of the market and have a volume of 32.5 million gal, valued at \$143 million.

The value of product shipments of soap and detergents is forecast by McIntyre to grow 2 to 3% annually through 1995. The heavy-duty liquid detergent formulations will hold market share of about 40%, he says. However, profit margins on liquid detergents will be lower than on powdered detergents because liquids cost more to make. They require more surfactant, as much as 40% of the total in some formulations compared with about 10% in conventional powdered detergents. In the case of phosphate-free formulated liquids, more costly substitutes for the phosphate builders are used to obtain water-softening properties. McIntyre adds that, barring discovery of a builder as cost-effective as phosphates, the phosphate-free detergents are unlikely to gain a major share of the U.S. market before 1995.

Outlook is for a 2% annual increase in demand for chemicals formulated into detergents by 1995, with volume reaching about 5.5 billion lb, McIntyre says. The fastest growing demand for chemicals will be in the specialty area for products that can substitute for phosphates by adding water softening and other properties to detergents.

The only detergent chemicals whose demand is declining are the phosphates, sodium tripolyphosphate (STPP) and tetrasodium pyrophosphate (TSPP). McIntyre estimates use of STPP will decline 3% annually over the next few years, because detergents containing phosphates are banned in more than 25% of the U.S. Debate rumbles on concerning the amount of eutrophication that can be traced to phosphates in detergents, despite some evidence that 80% of the problem stems from human wastes and commercial fertilizers. Last year, about one third of detergents sold were free of phosphates. Home laundry detergents accounted for about 17% of phosphate consumption. The remainder goes mainly into various cleaners.

Although they are more costly and less effective, zeolites substituted for phosphates have become more and more popular among formulators during the past three years.

Product Report

Other popular replacements in the powdered detergent market are sodium silicate and calcium carbonate. In addition to their other purposes in detergent formulations, enzymes also are being used as builders. Last year, \$100 million worth of enzymes showed up in detergent formulations, a sixth of the enzyme market, by value, and the largest single use, McIntyre says. Speculation is that, as almost all enzymes will be made by biotechnology by 1995, an enzymatic method of bleaching may be developed, further increasing use of enzymes in detergents.

Builders, as a class of detergent chemicals, will grow modestly during this decade, according to a report on the outlook for detergent chemicals from a project directed by William P. Weizer of Freedonia Group in Cleveland. Demand for builders will grow 1.5% annually on the average, from less than 2.9 billion lb in 1989 to about 3.1 billion lb in 1994, and to 3.3 billion lb by 2000. The slower growth for builders than for all detergent chemicals results from a shift toward more use of surfactants at the expense of builders, particularly for detergents that are made to be sold in areas where phosphate builders are banned.

Growth in use of other builders

such as sodium carbonate—soda ash—(2.0%), zeolites (8.8%), and sodium citrate (2.4%) will offset an average 1.2% annual decline in use of STPP in household detergents. Consumption of zeolites and sodium citrate, used in smaller volumes than sodium carbonate, in detergents in 1989 was some 1.1 billion lb. Use of sodium carbonate in all types of cleaning compounds was more than 1.6 billion lb, or between 11 and 12% of total U.S. use.

In detergents, soda ash functions as an agglomerating aid, a surfactant carrier, and a source of alkalinity, in addition to its builder activity. The shift toward concentrates or compacts also requires increases in density of the formulated detergents. As an example of supplier innovation to improve detergents, FMC now makes soda ash by the sesquicarbonate process as well as by the monohydrate process, says Jeffrey J. Prickel, soda ash product manager. As a result, FMC has the flexibility in special density intermediate grades to meet specific formulating needs of detergent makers.

The other nonphosphate builders are consumed in detergents in much smaller volumes. Detergent use of zeolites, for example, was 203 million lb in 1989, according to the Freedonia study. Growth is forecast to average 8.8% annually, with volume reaching 310 million lb in 1994 and 410 million lb in 2000, because of their substitution for STPP in powdered detergents. Because it is preferred for liquid formulations, use of sodium citrate will grow 2.4% annually, from 71 million lb in 1989 to 80 million lb in 1994.

Phosphate builders in cleaning products remain the best cost/performance value, various industry sources point out. Phosphates are a part of any formulation that is used as a standard of detergency, says Lewis G. Furman, marketing director of FMC's phosphorus chemicals divi-

sion. The phosphates are used in concentrates for a variety of reasons, not the least of which is the long experience that formulators have with them. This is why the compacts initially have come out as phosphate-built detergents, adds Dennis E. Knudson, FMC's product manager for detergent phosphates. This development may lead to increased use of phosphates.

In markets for detergents other than home laundries, phosphate builders have made some notable gains. Use of both home automatic dishwashing detergents and institutional dishwashing detergents has grown and has increased demand for phosphates modestly, says Michael J. Berezo, business manager for detergent intermediates at Monsanto. A shift in sales toward the concentrated powders also might help, but concentrates without phosphates currently are under development.

The strengthening demand for phosphates has brought supply and demand for phosphorus chemicals about in balance and has permitted a price increase for STPP of more than 8%, Berezo says. Current prices are 32.5 cents per lb, up from 30 cents, the level reached after a round of large price cuts in 1989.

Phosphates consumption in cleaners in 1990 declined about 5% from 1 billion lb in 1989, estimates FMC's Knudson. However, production didn't decline as much, because of the substantial gain in exports. In fact, the net of exports over imports has gained 180 million lb over the past five years. The export growth was especially large in 1989 resulting from declines in the value of the dollar. Global production and consumption of STPP now amounts to about 2.5 million metric tons annually, according to FMC.

Bans on use of phosphate builders in detergents continue to grow, however. Two states will be added to the list of total bans, according to the Soap & Detergent Association (SDA). At the beginning of January, the ban in Georgia was scheduled to go into force. On March 1, Pennsylvania will institute a ban. Opposition by SDA to restrictions or bans on use of phosphates remains based on sound scientific data that find no



Technician checks cleaning efficiency of dishwasher detergents at BASF's labs in Wyandotte, Mich.

Surfactants consist of four types

The surface activity, key to effectiveness of a surfactant, depends on the chemical makeup of the molecule. The large number of compounds that exhibit surface activity are classified by the charge on the surface-active moiety, generally the larger part of the molecule.

Anionics. These surfactants have a negative charge on the surface-active moiety. They account for about two thirds of total U.S. surfactant output. Most are organic acid salts of sodium and potassium; a much smaller number are salts of calcium, ammonia, or an organic amine. Nearly all soaps are anionics. Major examples:

- Carboxylates account for about a quarter of U.S. production of anionic surfactants. Most are salts of acids derived from natural products such as coconut or palm kernel oils and tallow.

- Sulfonates are more than half of anionic surfactant production. The major categories are dodecylbenzene sulfonate and lignin sulfonates.

- Sulfuric acid esters and salts are most of the remaining anionics. Chemically, most are salts of reactions of sulfuric acid with long-chain alcohols, some of which are ethoxylated.

Cationics. These surfactants have a positive charge on the surface-active moiety, usually on an amino or quaternary nitrogen. They are expensive surfactants because of high cost of reactants and processing. As such, produc-

tion is 5 to 10% of the total. Important chemical groups are:

- Amine oxides and other oxygen-containing amines, many based on natural or synthetic organic acids.

- Monoamines with long chains derived from natural oils, but not oxidized.

- Quaternary ammonium salts based on tallow or alkylbenzenes.

Nonionics. This diverse group of surfactants accounts for less than a quarter of U.S. production. Nonionics are solubilized by chains of ethylene oxide groups. They often may be used with other surfactants in formulations for very specific uses. Two major groups of nonionics are:

- Esters of carboxylic acids from natural and synthetic sources and mono- and multiglycols with long chains.

- Ethers made by ethoxylating linear alcohols and alkylated phenols.

Amphoterics. These surfactants represent a tiny fraction of total production, or about 0.6% of the 6.8 billion lb of surfactants produced in 1989. They are considered specialty surfactants and often are proprietary products offered for limited markets. Examples include:

- Alkylbetaines made from fatty acids and alkyldimethylamines.

- Imidazonilium derivatives from reaction of imidazolines and sodium chloroacetate.

proven water quality advantages to result from lower phosphate detergent loadings, says Theodore E. Brenner, SDA president. Brenner says that where presence of heavy metals in sewage is an issue, SDA will emphasize that new research has documented that the contributions of cleaning products to the overall heavy metal content are insignificant.

Increased use in both liquid detergents and in detergents without phosphate builders will result in a growth rate of 2.3% annually for surfactants formulated in household laundry and dishwashing detergents and in industrial and institutional cleaners, according to the

study by Freedonia. Consumption will reach 2 billion lb in 1994, up from less than 1.8 billion lb in 1989. If nonphosphate builders are improved, however, the growth rate may decline, as smaller amounts of surfactant are needed to get the desired cleaning performance.

It is no surprise that, because of their large volume, growth in use of anionic surfactants in these detergent markets will be lower, at 1.6% annually, than will be the 3.2% rate for the smaller-volume nonionics. The growth rate for amphoteric surfactants will be even higher at 5.5% annually, but from a tiny base of just 13 million lb in 1989. Nonionics use is expected to grow because demand

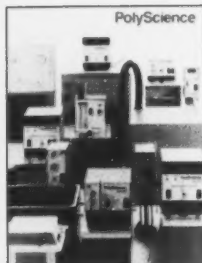
for cleaning products is shifting toward liquids. Nonionics are preferred in liquids because of the ease with which they blend into liquid formulations, their somewhat better resistance to effects of calcium and magnesium ions in wash water, and their better performance in cleaning clothes made with synthetic fibers.

Output of all types of surfactants declined in 1989 about 7%, from 7.3 billion lb in 1988 to 6.8 billion lb, according to a just-issued report of the U.S. International Trade Commission (USITC) on production of synthetic organic chemicals. Output in 1990 was expected to rise about 4%, to 7.2 billion lb. An additional small growth in production of 2% is forecast for this year, which would bring the total again to 7.3 billion lb, the record for production set in 1988.

As in the past, anionic surfactants have dominated the U.S. output, accounting for almost 66% of the total. Nonionics account for about 24% of production, with most of the remainder cationic. More than half of the anionic surfactants are consumed captively, largely in the manufacture of household laundry detergents and other consumer detergent products. These surfactants, commensurate with their large volume, have, at 32 cents per lb, the lowest average unit value for 1989 merchant sales. This value is below the average of 55 cents per lb for all surfactants sold in 1989, according to USITC.

Excluding soap, global consumption of surfactants in 1990 was about 16.3 billion lb, valued at \$3.65 billion, according to a new study by Colin A. Houston & Associates of Mamaroneck, N.Y. Consumption in the U.S. was about 30% of global consumption at 4.9 billion lb. Industrial uses of surfactants in the U.S. took more than 45% of the total. In the rest of the world, industrial uses accounted for 25% of consumption. The remainder of uses include household detergents, industrial and institutional cleaners, and personal care products. By the year 2000, the consulting firm predicts that global consumption of surfactants will reach 22 billion lb, and U.S. consumption will be 6.6 billion lb.

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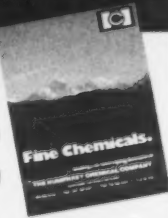
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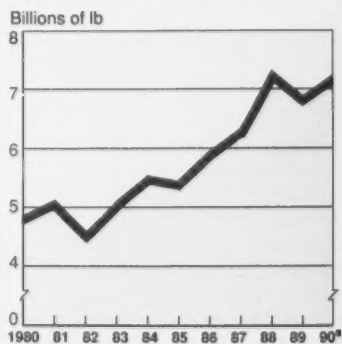
Product Report

Use of surfactants in household and personal care products in the U.S. will grow at an average of 1.3% annually between 1988 and 2000, says Marilyn L. Bradshaw, business manager at Colin A. Houston & Associates. Some new surfactants will come on the market in small volumes, but with high growth rates—such compounds as alkyl polyglucosides, methyl ester sulfonates, and paraffin sulfates. The traditional major-volume surfactants, such as linear alkylbenzene sulfonate (LAS), have stable demand. U.S. producers face increasing competition from production outside the U.S. (despite a 17.5% duty on imports), because of growing capacity around the world, according to Bradshaw.

Despite competition from other surfactants, LAS demand will grow in 1991, agrees Richard E. Lundgren, Monsanto's business manager for surfactants. This is the workhorse of the current large-volume surfactants and it will continue to hold its position because detergent and cleaner manufacturers have vast experience with formulations containing LAS and its proven safety in many use areas. The effect of changes in formulations on use of LAS will be minor this year, he concludes.

Longer term, however, greater use of enzymes and other additives likely will increase the use of mixtures of surfactants or could diminish the concentration of total surfactant in a formulation. Mixtures of surfactants in detergents offer two advantages

Organic surfactants output up but below 1988 peak



■ Estimated. Source: U.S. International Trade Commission, C&EN estimate

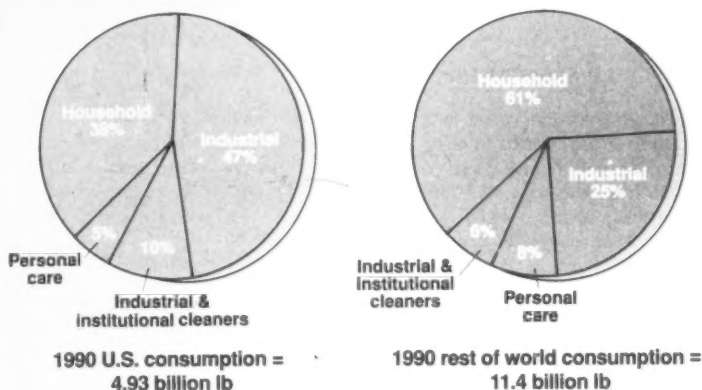
Product Report

to formulators. In most cases, mixtures are easy to change to meet changes in consumer performance demands. Mixtures also allow formulators to balance or to diversify costs of the surfactants they use.

Prices of raw materials for linear alkylbenzene (LAB) have become volatile as a result of Iraq's invasion of Kuwait. When benzene prices rose to \$2.00 per gal and kerosene prices more than doubled, LAB prices jumped 10 cents per lb in October, says W. Jan B. Vogel, a vice president of Vista Chemical. At the beginning of January, Vista added another 18.5 cents per lb to prices, but put a temporary voluntary allowance of 20.5 cents per lb in place for an effective decrease in price of 2 cents per lb.

In a similar fashion, prices were increased for surfactant materials based on ethylene, the U.S. prices of which increased from 22 to 30 cents per lb. In Europe, ethylene prices rose even more, going from about 25

U.S. surfactant use differs from rest of world

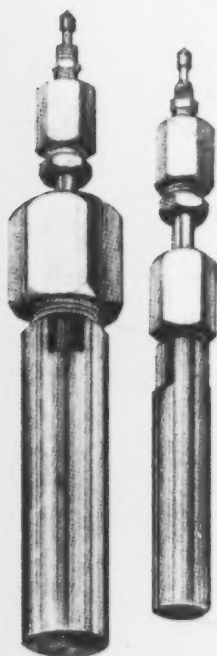


Note: Excludes soap. Source: Colin A. Houston & Associates

cents per lb to 40 cents per lb. Long-chain alcohol and ethoxylate prices also increased in October and again in January, but the January increases were offset by allowances on most products.

Natural oils (also major feedstock for surfactants) recently have become more costly, says Vogel. The

price increases reflect the energy component of the cost of producing and marketing the natural oils, often produced in tropical areas distant from consuming points. Prices of both coconut and palm oils increased in October from about 14 cents per lb to more than 17 cents per lb, putting pressure on prices of



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Nearly all industries use surfactants

Surfactants not formulated into detergents have applications in other major industries that produce goods. A study by Colin A. Houston & Associates indicates that industrial uses require nearly half of U.S. consumption of surfactants. But, because details of these uses are so fragmented, the volume consumed by each is uncertain.

These industries include:

- Food. Surfactants are used both as cleaners and emulsifiers in food processing. The surface-active properties are used either to generate or inhibit foams.

- Pharmaceutical. Serve as emulsifiers, dispersants, and synergists for active ingredients.

- Agriculture. Used as emulsifiers (wetting agents) must not react with active materials. They must be biodegradable and have low phytotoxicology. Some are used to prevent caking of fertilizers during mixing and to improve uniformity of distribution.

- Textile. Formulated more often into detergents than in other industrial uses, aid cleaning of natural fibers, reduce friction in spinning and weaving, improve application of finishes, aid dyeing, and minimize static charge.

- Chemical. Aid reactivity by their

emulsification property, such as in polymerizations or hydrolyses.

- Plastics. Widely used in fabrication of plastic products such as foams, molded items, extrusions, and microcapsules.

- Paint. Aid these products, that are basically dispersions, by speeding the milling of dyes and mixing of ingredients, by maintaining stability, and by aiding the leveling of powder coatings.

- Pulp and paper. Used to help remove the cellulosic pulp from other components of wood, to reduce foam during papermaking, and to aid deinking and removing additives from recycled paper.

- Mining and ore processing. Aid dust-binding agents and act as frothing agents that hydrophobize the valuable minerals.

- Petroleum production. Used in drilling fluids to disperse and carry cuttings and are used to improve production by breaking water-oil emulsions and to aid water or other flooding of oil-bearing formations.

- Other industries using significant quantities of surfactants include tanning, fur processing, photography, metal processing, electroplating, adhesives, construction, and firefighting.

alcohols and derivatives made from these oils.

The change in pricing for basic raw materials worldwide is an integral part of the overall, mushrooming changes in global operations that companies in the detergent industry face. Other than pricing concerns and new product introduction, new markets are developing as older markets expand. For example, in 1990, Vista recognized strong growth in demand for LAB coming from its increased consumption for detergents and detergent intermediates in Eastern Europe, explains Vogel. Many industry sources anticipate further expansion of this market and others in developing countries during this decade.

Multinational companies with access to the existing research and marketing organizations at home and abroad should be well positioned to handle the largely uncer-

tain future of the evolving global market, says Kenneth R. Schoene, director of performance chemicals at BASF. His company has adopted "world industry-segment teams" aimed at harnessing its global resources to develop products that can meet the increasingly complex needs of detergent manufacturers. One result of BASF's product and applications research will be to introduce, during 1991, both multifunctional and soil-specific polymers and surfactants for these evolving needs, Schoene adds. Such focused activity by industry suppliers is expected to produce notable gains in raw materials that meet environmental and performance concerns.

Detergent formulators and suppliers of materials are bringing almost constant change to demand for different components, as they improve performance and lower costs while

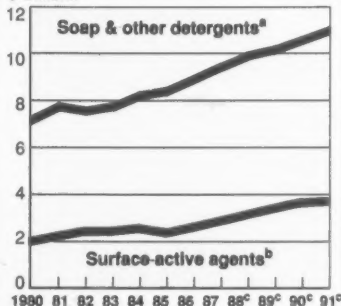
meeting new and anticipated environmental regulations. Surfactants, for example, are constantly under development, especially those that are mixtures of several similar compounds. The change from branched chain alkylbenzenes to linear alkylbenzenes in the early 1960s, to speed biodegradation of the surfactant, proved that both small and major changes in composition of molecules for performance reasons will be accepted, paid for, and spur the search for still better performance.

Extensive changes in average composition of big-volume products such as household laundry detergents are rare; changes are more evolutionary. For example, LAS continues to hold its share of the surfactant content in laundry detergents while improvements are being made in the quality of competing surfactants, such as those based on detergent or long-chain alcohols. But the position of LAS depends heavily on comparison of its cost relative to the cost of competing surfactants—the long-chain alcohol derivatives such as the ethoxylates, sulfates, and ether sulfates. Time is needed to affect compositions, but the relative costs of basic petrochemicals, such as benzene and ethylene, and of natural fats and oils, eventually will influence surfactant composition in household and other detergents.

Manufacturing cost and performance, in conjunction with other components of a detergent, partially offset consideration of the raw material costs in making a choice of surfactants. One favorable manufacturing cost factor for LAS is its ease of spray drying, a step in making powdered detergents. If a phosphate builder can be included in the formulation, then LAS likely will be used because the builder covers its greater sensitivity to water hardness than either alcohol ethoxylates or alcohol ether sulfates. However, in liquid heavy-duty detergents made for clothes washing, LAS content is reduced by replacing it in part with alcohol ethoxylates—no phosphate builders are used in liquids because they can cause a performance problem. In combination, LAS and alcohol ethoxylates appear to have a synergistic effect that permits use of

Value of cleaning products shipments will slow

\$ Billions



^a Standard Industrial Code 2841. ^b Standard Industrial Code 2843. ^c Estimated. Sources: Department of Commerce, C&EN estimates

a smaller amount of surfactant than might otherwise be needed in heavy-duty liquids.

Most light-duty liquid detergents, such as those used for hand dishwashing, have LAS as the major surfactant. Usually, alcohol ether sulfates also are used to give better grease removal and to make the product less harsh to the skin. Although liquid automatic dishwashing detergents are growing rapidly from a small base, most continue to be powders. Therefore, the light-duty liquid detergent use of LAS has remained level or has declined during the past few years. Additional, but not strong, competition comes from alcohol sulfates.

The alcohol derivatives used as surfactants go into many other products, especially personal care items such as shampoos. The alcohols are obtained either from natural products or are made synthetically from petroleum hydrocarbons. Cost of the basic raw materials influences whether natural or synthetic alcohols are used, subject to performance considerations. Sizable quantities of these derivatives are either formulated into various industrial and institutional cleaners or are used largely unformulated in industrial processes.

Many other surfactants are formulated into soaps and detergents. Most are expected to increase in demand during the nineties at long-term rates above average, because their volumes are small when com-

pared with volumes of LAS or major alcohol derivatives. These smaller volume surfactants include the anionics, α -olefin sulfonates, and alkyl glyceryl ether sulfonates, all of which are used mostly in personal care products. Others are the nonionics, which are various ethoxylated alkyl phenols used in limited amounts in laundry detergents and household cleaners (the bulk goes into industrial cleaners), the fatty alkanolamides used in light-duty dishwashing detergents, in various personal care products, and in industrial and institutional cleaners, and the fatty amine oxides, going mostly to light-duty dishwashing detergents.

Less shifting between components of formulated detergents, especially surfactants, is expected because of efforts by suppliers to develop quality and performance standards. Suppliers are moving toward specified systems and guaranteed performance, says William R. Kristoff, Rhône-Poulenc's marketing director for surfactants and specialty chemicals. Suppliers are offering more service each year, especially in quality control. Such trends tend to reduce a customer's flexibility in changing raw materials, and cause potential suppliers more difficulty in entering a market.

In addition to surfactants and builders used in detergents for various reasons, numerous other components are important. These include bleaching agents, fabric softeners, enzymes, optical brighteners, anti-redeposition agents, fragrances, and fillers or diluents. As a group, detergent materials used in household detergents and in industrial and institutional cleaners (other than builders and surfactants) amounted to about 5% of total chemical consumption in 1989, according to the study by Freedonia.

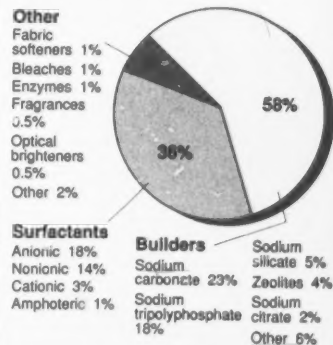
Some of these small-volume products will have high growth during the early 1990s. For example, use of enzymes and bleaches will grow more than 10% annually because of the popularity of multifunctional detergents. Consumption of fabric softeners is forecast to grow about 5% annually, again aided by the popularity of multifunctional detergents. As a group, the other smaller

volume detergent additives will grow more slowly. In the group, some specialty products, such as water-soluble polymers, could grow faster because of their multifunctionality as both builders and anti-redeposition agents.

Because of consumer preference for detergents that handle stains and odors better, much development work continues to improve bleaching. Enzymes have found an important niche in formulated detergents that meet these newer consumer laundry requirements, but nearly all enzymes suitable for handling stains and other soils are deactivated by chlorine bleaches—the various hypochlorites. As substitutes for chlorine bleaches in detergents, oxygen bleaches have been around for a long time and became commercially significant in home laundry during the past decade. They will continue to grow, albeit slowly.

By far, most oxygen bleaches used in detergents, or alone, are sodium perborates. In the U.S. a shift toward lower temperatures for washing clothes has hurt use of perborates bleaches, because their efficiency declines significantly with temperature. To improve the efficiency of perborates in cool or even cold water washing, both the suppliers of perborates and other companies have worked on bleach activators. So far, success has been limited, from a cost and performance view-

Many chemicals find diverse uses in detergents



Total 1989 consumption = 4.89 billion lb

Source: Freedonia

Product Report

point. Most bleach activators are acylating agents that react in a nucleophilic substitution with hydrogen peroxide anions in the washing liquor. These activators—complex organic chemicals—work stoichiometrically; therefore they must be present in relatively large quantities at costs too great for full activation. If activators are used in limited quantities, then only partial activation is achieved, but it often is sufficient to meet performance requirements at an acceptable cost.

The shift toward concentrated detergents for all kinds of cleaning allows strong growth for active oxygen bleaches in formulations designed to give high performance, says Frank E. Caropreso, FMC's detergent industry manager for peroxygens. Sodium perborate is being incorporated more into automatic dishwashing detergents, as formulators attempt to eliminate chlorine from these products. This bleach, as well as other peroxygens, are being considered for formulations aimed at the various industrial and institutional cleaner markets, he says.

R&D appears to be widespread on ways to activate and stabilize peroxygens in home laundry and automatic dishwashing formulations and in the industrial and institutional cleaners, including liquids. At FMC, the research focuses on finding multifunctional peroxygen carriers. So far, two promising, but undisclosed, candidates have been found in the laboratory, according to Caropreso. The concern over chlorine oxidation is expected to spur work on stable peroxygen compounds for various kinds of cleaning compounds.

Both hydrogen peroxide as a liquid bleach added directly to the washing liquor, and solid active oxygen compounds put into detergents for clothes washing, are growing well. Incentive for adding hydrogen peroxide stems from efforts to improve stain removal without damage to color or fabric. Many of the liquid bleach formulations include a surfactant added to provide greater efficacy. Another development is the use of peracetic acid, with hydrogen peroxide added, to be an acetic sanitizer in hard-surface cleaners supplied to the industrial and institutional markets of food and beverage

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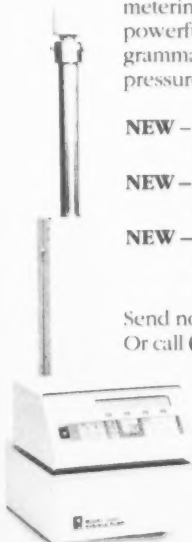
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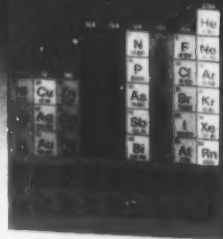
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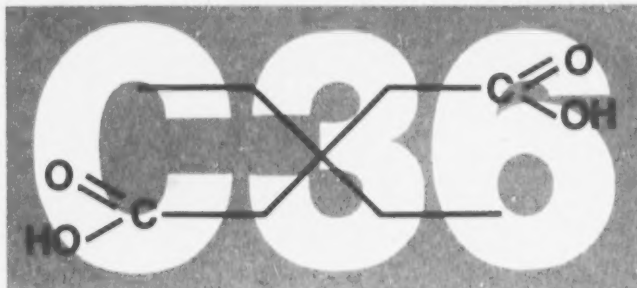
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CIRCLE 23 ON READER SERVICE CARD

Product Report

processing. The product is also used in medical equipment sterilization.

Initially, sodium perborate was supplied to detergent formulators as the tetrahydrate. More recently, a monohydrate form became available from foreign sources and is getting wide use. The monohydrate provides a higher oxygen content (15% versus 10% for the tetrahydrate), better stability and compatibility with other ingredients (including formulations containing low phosphorus content or no phosphorus), and more rapid dissolution at lower temperatures.

This month, Du Pont will begin the first U.S. production of sodium perborate monohydrate at Memphis, Tenn., says Phillip M. Richardson, market manager for cleaning products. Du Pont will dedicate a part of the plant's tetrahydrate capacity to supply more than 30 million lb per year of monohydrates. Richardson calls this the first phase of adding monohydrate capacity to meet a growing demand in North America and in the world. He estimates that the demand for the monohydrate form in North America will increase between 60 million and 80 million lb per year in the next five years.

Numerous other additives are now required in the various kinds of detergents and cleaners offered to all segments of consumers. All are added to provide a unique function, although some act synergistically with each other. How much these materials are used in detergents and other cleaners is uncertain because, in most cases, other uses account for significant shares of production. Frequently, details of production are not reported, because only a few companies make these materials, and the volume is very small.

Enzymes, one of these small-volume substances, are incorporated increasingly into laundry detergents. Their ability to improve cleaning has been known for more than 75 years. A variety of problems, including difficulty of producing in high volume, limited wide use of enzymes until the 1980s. Most enzymes used in detergent formulations are proteases and amylases of proprietary forms.

Enzymes are added to detergent formulations, especially liquids, to

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Product Report

attack proteinaceous soils, which most often appear on clothes as stains. After drying and aging, these stains strongly resist action of most low-cost and high-volume surfactants. The enzymes are then added, to attack hydrolytically a peptide or ester bond in the protein, thereby either destroying it or making the fragments easy for a surfactant to remove. Enzymes for detergents are expensive, costing over \$6.00 per lb, according to Hans C. Kuenzel of Freedonia.

Fabric softeners are forecast by Freedonia to be the third fastest growing detergent additive after bleaches and enzymes. Demand for these materials will be increasing about 5% annually through 1994 to about 47 million lb. Part of the increase in use of fabric-softening additives stems from new materials that are added to multifunctional detergents. Quaternary ammonium compounds have been used as fabric softeners for some time because they are adsorbed on negatively charged textile fabric surfaces, but a wide variety of new compounds are now used in both postrinse softeners and in the multifunctionals. Other components of postrinse softeners include whitening agents, preservatives, dyes, and fragrances.

Of the miscellaneous additives in a laundry detergent formulation, one of the most important to high performance is an antiredeposition agent. To the average consumer, the best measure of poor washing performance is "greying" of the fabrics, largely a result of part of the dirt's being redeposited. For more than 50 years, sodium carboxymethyl cellulose, as an antiredeposition agent, has been known to be effective on cotton fabrics, but less so on synthetics.

Newer products added to detergents as antiredeposition agents include, for example, conventional surfactants, nonionic cellulose polymers, and polycarboxylic acids. Although the volume of water-soluble polymers used in detergents for antiredeposition agents and other functions isn't large, it is enough to spur BASF to add capacity to its plant at Spartanburg, S.C., early this year. Polymers from BASF are designed for such diverse uses as a soil

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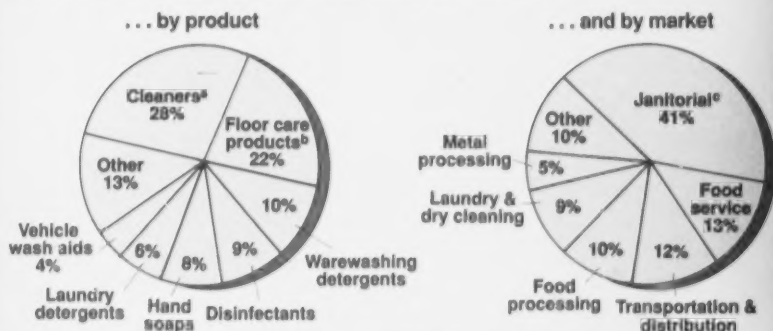


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CIRCLE 16 ON READER SERVICE CARD

Product Report

Industrial and institutional cleaning chemicals



Total 1989 consumption = \$3.68 billion

a Alkaline, solvent, acid, and general purpose. b Waxes, polishes, spray buffs, strippers, sealers, carpet shampoos, and spotters. c Includes retail, health care, industrial and office, and contract cleaners. Source: Freedonia Group

shield in laundry detergents or increasing effectiveness of hard-surface cleaners, says Schoene. Further research is expected to bring out other multifunctional and soil-specific polymers this year.

Foam stabilizers as additives to detergents work both to increase and decrease the foam, depending on the application. Most light-duty liquids contain a soap to increase foam that works well with LAS surfactants. For automatic dishwashers, low foaming is needed. So, to depress foam, organic compounds that may interact with calcium ions are added.

In most home clothes washing a "blueing" agent no longer is added to the rinse. Consumers now expect whiteness from the detergent. As a result, use of optical brighteners continues to grow in home and industrial and institutional laundry detergents. The "blueing" agent, a dye, ultramarine blue, has worked well on cotton fabrics since its discovery in the 19th century. But with synthetic fibers, the dye works less well. As a result, optical brighteners—or fluorescent whitening agents—work as dyes to convert invisible ultraviolet light to visible light. Basic structures for these complex organic compounds include stilbene and derivatives, coumarin, quinolone, pyrazoline, and benimidazole. Acting as a dye does, these agents bind to the fiber by hydrogen bridges. Their properties that are important to good performance are an affinity for the fiber

and stability and resistance to oxygen, light, and chlorine.

A wide range of other additives go into laundry detergents. Solubilizers that aid solubility of the surfactant and control viscosity, include ethanol, glycol ethers, or sodium xylene sulfonate. Corrosion inhibition is obtained if sodium silicate is added as a builder. If not used as a builder, it may be added in small quantities to inhibit corrosion. Perfumes, or fragrances, are added both to overcome the detergent's odor and to provide a favorable scent when the clothes are ready to wear. Fillers, diluents, and processing aids make up the remainder of the formulation. The shift toward concentrates of various kinds is leading to a reduction in the amount of filler and diluent in most formulations.

Household detergents and cleaners will remain the largest market for detergent chemicals, although industrial uses of surfactants could grow faster than other uses over the decade. Growth in the industrial and institutional cleaner market is second fastest, with personal care products last and smallest. Personal care products, however, are forecast to continue their slow growth unabated during the recession because this area of detergent chemicals is considered to be recession-proof.

The industrial and institutional markets take about a quarter of the detergent chemicals consumed in the U.S., excluding those that go



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Product Report

into personal care products and industrial nondetergent markets, according to the Freedonia Group study. These markets used 10% of surfactants in 1990, or nearly 500 million lb, estimates Bradshaw at Colin A. Houston & Associates. These markets cover consuming areas such as cleaners of many kinds, floor care products, warewashing detergents, disinfectants, industrial laundry detergents, hand soaps, and vehicle washing detergents. The remaining 90% goes into household cleaners, personal care products, and industrial uses.

The industrial and institutional cleaners market with sales of more than \$1 billion in 1989 will grow more slowly than other smaller segments of the total market. Considerable shifting in the kinds of cleaners used will occur through 1994, forecasts Freedonia. Use of alkaline cleaners, for example, will grow slowly because other kinds of specialty cleaners will be substituted for them. Acid cleaners also will grow more slowly because of stagnation in dairy farm use and slowness in metal-processing markets resulting from the reduction of durable goods manufacture during the recession.

The floor care markets are expected to grow because there is better acceptance of new formulations that are used with higher speed burnishing equipment and that otherwise save labor by easing application and increasing durability. More formulations prepared for specific application equipment will further help demand in the early nineties.

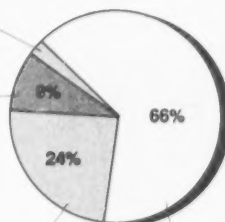
Detergents for these and the other smaller uses also are being reformulated for further use of automated dispensing or other application equipment. This kind of equipment helps hold down costs because it permits more accurate dosing, minimizes spills, and minimizes employee contact. Vehicle washing is one of the specialized areas in which detergents are being reformulated to meet requirements such as the very high recycling of water and minimal

Anionics dominate output of surfactants

Amphoterics 1%

Cationics

Amines without oxygen & salts 3%
Quaternary ammonium salts without oxygen 2%
Amine oxides without amide linkages 2%
Amine oxides with amide linkages 1%
Other 1%



Nonionics

Ethers 17%
Carboxylic acid esters 5%
Carboxylic acid amides 1%
Other 1%

Anionics

Sulfonic acids & salts 35%
Carboxylic acids & salts 16%
Sulfuric acid esters & salts 14%
Other 1%

Total 1989 production = 6.79 billion lb

Source: U.S. International Trade Commission

effluent through use of on-site treatment of waste wash waters.

Some of the industrial markets that are very specialized offer huge growth potential. Recycling paper fibers is an example. Last year, only about 50 million lb of surfactants were used in deinking and other processing of recycled paper, says Denise C. Galanci, market manager for surfactants for Union Carbide. Estimates of future demand are difficult to obtain because of the unsettled timetables for completion of the large number of new deinking plants announced throughout the U.S. Handling carbon and colorant particles, fillers, and other materials removed from the paper also offers large potential markets for flocculants, as well as other chemicals. Technical service from suppliers to recyclers will flourish as this detergent use grows.

The industrial and institutional detergent markets best exemplify the future outlook for the industry through increasingly complex formulations to meet consumer demands. As a result of demand by consumers for new products, change will continue in the soap and detergent industry. Although no innovation as significant as the introduction of concentrated detergents is expected this year, many noteworthy developments will be made. And they will continue to be made. □

CIRCLE 45 ON READER SERVICE CARD

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